

PART I
THE REACTION OF HYDRAZOIC ACID WITH SOME
UNSATURATED COMPOUNDS

PART II
THE AROMATICITY OF N-METHYL-2-PYRIDONES

BY
JACK SYLVESTER HINE
B. S., University of Arkansas, 1944

AN ABSTRACT OF A THESIS
SUBMITTED IN PARTIAL FULFILLMENT OF THE REQUIREMENTS
FOR THE DEGREE OF DOCTOR OF PHILOSOPHY IN CHEMISTRY
IN THE GRADUATE SCHOOL OF THE
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PART I

THE REACTION OF HYDRAZOIC ACID WITH SOME UNSATURATED COMPOUNDS

INTRODUCTION

Schmidt and Klavehn¹ have stated that in the presence of strongly acidic catalysts hydrazoic acid reacts with unsaturated compounds to form Schiff bases. In the current investigation the reaction of hydrazoic acid with certain unsaturated compounds not used by Schmidt and Klavehn was carried out.

DISCUSSION OF RESULTS

A number of unsaturated compounds were treated with hydrazoic acid in the presence of concentrated sulfuric acid and other acidic catalysts. From the reaction with cyclohexene no pure products were isolated. The reaction with indene and with indene dibromide yielded only polymeric substances. Only unchanged starting material was isolated from the reaction with tetraphenyl-ethylene. The reaction with stilbene yielded diphenyl acetanilide, aniline, benzaldehyde, and probably phenyl acetaldehyde.

An attempt to bring about the addition of hydrazoic acid to benzalacetophenone was unsuccessful.

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PART II

THE AROMATICITY OF N-METHYL-2-PYRIDONES

INTRODUCTION

The structure of N-alkyl-2-pyridones is usually written

as 1-alkyl-2-oxo-1,2-dihydro-pyridine. However, electronic structures for these compounds may be written in which the pyridine ring contains the three conjugated double bonds of a typical aromatic six-membered ring. The purpose of the present research was to investigate the preparation, properties, and reactions of 2-pyridones and their N-substituted derivatives with particular reference to their aromaticity.

HISTORICAL

A number of workers have discussed the structure of 2-pyridones. The structures have been investigated by means of the ultraviolet absorption spectra,^{1,2} indices of refraction and dispersions,³ and other physical properties as well as by investigation of the chemical reactions. All of the workers agree that the active hydrogen atom is attached, largely at least, to the nitrogen atom, and that the parent compound thus has the atomic configuration of 2-oxo-1,2-dihydro-pyridine. A variety of methods of preparation of 2-pyridones has been described. N-substituted 2-pyridones have been frequently prepared from the parent pyridone, but a number of other methods are available for their synthesis.

Several aromatic substitution reactions have been carried out on 2-pyridone and its N-substituted derivatives. In these reactions substitution has been shown to take place in the 3- and 5-positions.

DISCUSSION OF RESULTS

Oxidation of the 1,3-dimethyl-pyridinium ion by means of potassium ferricyanide in sodium hydroxide solution has been shown to yield 1,3-dimethyl-2-pyridone. The structure of this compound was established by comparison with 1,3-dimethyl-2-pyridone prepared from 3-methyl-2-pyridone.

A number of Friedel-Crafts acylation reactions were attempted on 1-methyl-2-pyridone without success. Neither 1-methyl-2-pyridone nor 2-pyridone was found to undergo

nuclear substitution when heated with benzoyl chloride in pyridine.

The Fries rearrangement of 2-pyridyl benzoate was shown to yield 5-benzoyl-2-pyridone. The structure of this compound was established by comparison with 5-benzoyl-2-pyridone prepared from 2-pyridone-5-carboxylic acid through the acid chloride via the Friedel-Crafts reaction.

The reaction of triphenylmethyl chloride with 2-pyridone was shown to yield a compound which is believed to be 5-triphenylmethyl-2-pyridone. The same compound was also shown to be formed by the reaction of 1-methyl-2-pyridone with triphenylmethyl chloride.

The following reactions were attempted without success: The thiocyanation of 2-amino-pyridine. The coupling of *p*-nitrobenzenediazonium chloride with 1-methyl-2-pyridone. The nitrosation of 1-methyl-2-pyridone. The preparation of addition compound of 1-methyl-2-pyridone with acetyl chloride, acetic anhydride, methyl iodide, and benzyl chloride.

An addition compound was prepared from 1-methyl-2-pyridone and dimethyl sulfate, but was not characterized.

The preparation of 2-methoxy-pyridine-5-sulfonamide from the corresponding 2-chloro- compound was accomplished.

Evidence has been presented to show that when 2-methoxy-pyridine-5-sulfonamide is heated it rearranges to 1-methyl-2-pyridone-5-sulfonamide.

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VITA

The author was born at Rockwell Field, California on July 2, 1923. He attended a number of elementary and secondary schools and was graduated from Central High School in Muskogee, Oklahoma in June, 1940. He entered the University of Arkansas in September of the same year and completed his undergraduate study there in December, 1943. He received the degree of Bachelor of Science in June, 1944. He was employed as an Assistant Research Chemist by the Cities Service Oil Company in Okmulgee, Oklahoma from December, 1943 until October, 1945. In the same month he entered the Graduate School of the University of Illinois. He held a University Scholarship until the following June, and University Fellowships from that time through September, 1947.



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